

THERMAL UPGRADING OF PETROLEUM RESIDS USING POLAR H-DONOR SOLVENTS

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INTRODUCTION

As a novel approach to upgrading petroleum resids it was proposed that experiments should be carried out utilizing polar H-donor solvents (e.g. tetrahydroquinoline (THQ) and indoline) in an effort to increase H/C ratio, increase desulfurization and demetallation, and improve the boiling point distribution to 90% boiling below 1000°F.

The objectives of this project were as follows: 1) To identify potential hydrogen-donating solvents for upgrading petroleum resids. 2) To screen these solvents and compare their effectiveness in improving the boiling point distribution and elemental composition of the resids. 3) Once the initial screening has been done, to fully test one or two of the best solvents in larger batch reactors, to fully analyze the effectiveness of the solvent. 4) To undertake model compound and solvent reactions and modeling to understand the H-transfer efficiency, docking interactions etc.

This paper will discuss the major findings for these objectives and make conclusions as to the potential use of H-donors in upgrading heavy petroleum resids.

EXPERIMENTAL

All reactions were carried out in 25ml microautoclaves and a 300ml batch reactor (Marathon Oil Co.). Petroleum resids were obtained from Marathon Oil and potential solvents were obtained from various chemical companies. In each reaction, a measured amount of resid/pyrene was weighed into the reactor along with a carefully weighed amount of solvent in various wt/wt (or mol/mol) proportions. The reactor was purged twice with nitrogen and pressurized to either 200psi with nitrogen (inert atmosphere) or 500-1500psi hydrogen. The reactor was then lowered into a fluidized sand bath set at a pre-defined temperature (375-450°C) for a pre-determined reaction time (60-180 minutes). After the reaction time had expired, the reactor was removed from the sand bath and immediately quenched in cold water. The reaction products were extracted with THF and hexane to determine conversion of the asphaltene fraction of the resid. The products were analyzed by gas chromatography to determine conversion of the solvent, and simulated-distillation (SIMDIST) to determine the boiling point distribution. Elemental analysis was carried out to determine C, H, and S.

RESULTS AND DISCUSSION

Thermal Cracking of vacuum resid (VR1) using Donor/Non-donor Solvent

In order to stop retrogressive reactions that occur during thermal cracking of resids, several experimental approaches can be undertaken: 1) Use molecular hydrogen to try and cap the reactive radicals which are recombining, 2) Use molecular hydrogen and a catalyst to improve conversion levels, 3) Utilize solvents that can be a source of hydrogen for radical capping and hydrogenation of aromatic rings. In order to assess these approaches, a study into vacuum residue (VR1) upgrading using various donor/non-donor solvents, hydrogen vs. inert atmosphere, and the impact of a catalyst on the reaction, was undertaken. The major results are shown in Figure 1, which gives conversion of asphaltene data and boiling point (by simulated distillation) data (<400°C and <550°C). Use of non-donor solvents (naphthalene, toluene, quinoline) in the reaction leads to retrogressive reactions, similar to those seen when no solvent is used. Tetralin (low polarity H-donor) does give up some hydrogen to cap the reactive radicals but the asphaltene fraction is not converted as much as when THQ (highly polar H-donor) is used. Hydrogen atmosphere does increase conversion of asphaltenes, but the use of a catalyst precursor, ammonium tetrathiomolybdate (ATTM), does not significantly improve the results. Quinoline (polar non-donor) is effective only when ATTM and hydrogen are present. This is due to the hydrogenation of quinoline to THQ which then acts as a donor. This idea of hydrogen shuttling between gas phase hydrogen, quinoline, THQ and the resid molecules will be discussed in detail later in the paper. Figure 1 also shows the effect of increasing THQ concentration of the solvent system on conversion and boiling point distribution. When 100% toluene is used, retrogressive reactions are occurring, leading to a negative conversion of 36%. As THQ is added to the solvent, conversion increases. With 100% THQ, asphaltene conversion increases to +30%.

One of the interesting features of Figure 1 is that there appears to be a relationship between asphaltene conversion and conversion of the resid to <400°C and <550°C material. This can be seen more clearly in Figure 2, where these two parameters are plotted against each other. It can be seen that as the heavier asphaltene molecules are converted to hexane soluble material, the amount of cracking to lower boiling products, decreases. There are some exceptions, which are pointed out in Figure 2 as catalytic reactions. The results suggest that there may be two mechanisms that need to be separately addressed when considering upgrading resids. Firstly, thermal cracking of side chains from the multicyclic compounds that make up a large proportion of these resids and cracking of smaller molecules to produce the distillable material, and secondly, hydrogenation and subsequent cracking of large polycyclic macromolecules that make up the asphaltene structure. To convert asphaltene requires hydrogen, which also reduces cracking of smaller compounds due to reactive radical capping. In a real process, it would be necessary to reach a compromise in conversion of asphaltenes and production of distillates. This would depend on the final product requirement. For example, in the case of resids, it may be important to produce a product that can be fed into the FCC for further treatment.

Thermal cracking of ROSE pitch using THQ

After the initial screening studies using VR1, it was decided to switch the initiative of the research to ROSE pitch. This was partly due to the fact that ROSE pitch is more difficult to upgrade and whatever we could achieve with this material we could probably repeat with the vacuum resid. ROSE pitch also contains a larger proportion of asphaltenes which have to be converted in order for the process to work efficiently.

The experimental approach was to determine the effect of temperature and hydrogen pressure on conversion of asphaltenes and cracking of the pitch to distillable products. Table I shows boiling point data, asphaltene conversion, solvent conversion and H/C ratio for ROSE pitch products under various reaction conditions. Asphaltene conversion is at a maximum at 425°C (33%). At 450°C, conversion drops to 24%. This is due to coking reactions occurring at this elevated temperature. From the boiling point data, it can be seen that as reaction temperature increases the amount of distillable products increases. At a reaction temperature of 450°C, 64% of the reaction products boil below 1000°F. However, an optimum temperature of 425°C was chosen for ROSE pitch based on asphaltene conversion and also at 450°C, there is evidence that THQ degrades via ring-opening, which would render the solvent useless for recycle. The results show that increasing hydrogen pressure does not have a great effect on cracking of the pitch to distillable. There is a significant difference in conversion of asphaltenes with increasing hydrogen pressure, and variation in solvent composition. This backs up the idea that we are dealing with two distinct reactions and mechanisms. Asphaltene conversion needs hydrogen to saturate the aromatic rings before they can be cracked. Cracking of side chains is more of a purely thermal process which is not as sensitive to increase in hydrogen pressure, but is sensitive to hydrogen donation ability of donors.

The initial H/C value of ROSE pitch is 1.27. At 375°C, H/C increases to 1.46. As reaction temperature increases to 400-425°C, there is the onset of major thermal cracking, which gives a further increase in H/C to 1.54. At 450°C, the increase in thermal cracking, is counterbalanced by a decrease in aromatic ring hydrogenation (thermodynamically limited). Also, there is probably major hydrocarbon gas production (methane, ethane) at 450°C, which decreases the H/C ratio of the products. When molecular hydrogen is used in the reaction system, H/C ratio increases to 1.62 (thermodynamics more favorable for hydrogenation of rings).

It has been postulated before that when considering the upgrading of resids, two distinct reactions have to be accounted for. Firstly, the behavior of the heavy asphaltene fraction, and second, the cracking of the lower molecular weight compounds. To explore this idea, the ROSE pitch was separated into hexane-soluble (oil) and insoluble fractions (asphaltene) and reacted separately. The products were analyzed by elemental composition and SIMDIST. The data are shown in Table I. By upgrading the ROSE pitch without the asphaltene fraction, it is possible to achieve a product which has a high H/C (1.70). We now know that we are achieving good products from the hexane-soluble fraction of ROSE pitch, but the question remains, what are we doing to the asphaltene molecules. At 425°C, 1000psi hydrogen, and 120 minutes reaction time, only 8% of the asphaltene fraction is converted to <800°F material, compared to 19% conversion from the oil fraction. 34% asphaltene conversion to <1000°F material is achieved under the same conditions compared to 36% oil conversion to <1000°F. This data is somewhat misleading, because a close look at the chromatograms obtained through SIMDIST, shows a different product distribution. Asphaltene molecules are converted to primarily 'pre-asphaltenes' shown by a hump in the chromatogram. The oil fraction is converted primarily to lower boiling compounds, e.g., alkanes.

Product evaluation of solvent donor experiments in stirred-tank reactor

Figure 3 shows how the <1000°F component concentration and contaminant removal varies with hydrogen consumption (measured by hydrogen donation from the solvent). Extrapolation shows that a hydrogen consumption of 4000-4400 scf/bbl of pitch will be required to obtain products of commercial interest, that is, products exhibiting <1000°F contents of 80-90 wt%.

During the upgrading of ROSE pitch with THQ at 425°C and 1000psi hydrogen, 38% of the sulfur was removed as hydrogen sulfide. This gives a final sulfur wt% of 3.7 (feed=6.0%). Of this 3.7 wt%, 8.8, 5.7, 40.7, and 44.6% of the unconverted sulfur was retained in the <460°F, 460-484°F, 484-1000°F, and >1000°F respectively. Calculation gives a product boiling less than 1000°F having a sulfur concentration of 2.1wt%. Therefore, the lighter products would still have to be further treated to remove the sulfur to acceptable levels.

Figure 4 shows the boiling point distribution of upgraded ROSE pitch at 425°C for various reaction times. At 425°C, conversion of pitch was essentially completed after 97 minutes. The stop in conversion is probably due to the equilibrium conversion of THQ to quinoline, i.e., hydrogen transfer stops once THQ and quinoline have reached equilibrium conversion. Once all the available hydrogen is used, retrogressive reactions will set in, leading to coke formation. It may be possible to increase conversion at 425°C, if hydrogen availability is increased. This could be achieved by increasing the solvent to resid ratio or increasing the hydrogen pressure. If successful, hydrogen consumption may exceed 4000 scf/bbl, which could give a <1000°F component concentration approaching 90%. This should also lead to a greater removal of contaminants.

Hydrogen transfer from various solvents to pyrene

To determine the hydrogen transfer ability of various polar solvents, pyrene was used as a model reactant. Table 2 shows the pyrene/solvent conversion data for these compounds (dihydropyrene is the only major pyrene hydrogenation product under these conditions). It can be seen that in terms of pyrene conversion, THQ and indoline are the best H-donors. However, in terms of hydrogen-transfer efficiency (solvent conversion compared with pyrene conversion), THQ is the better candidate. This prompted a closer look at H-transfer from THQ to pyrene.

Figure 5 shows how pyrene and THQ conversion, and H-transfer efficiency vary with hydrogen pressure. At low pressure (0-500 psi), H-transfer is 50% efficient. There could be

different explanations for this value. Thermodynamics (equilibrium conversion) could limit the hydrogenation of pyrene. Another reason for achieving only 50% efficiency can be explained if the docking reaction between THQ and pyrene is looked at more closely. Two of the hydrogens will be donated from THQ to pyrene to produce dihydropyrene. As they are transferred, THQ will become unstable and will have to release the remaining two hydrogens to produce the stable molecule, quinoline. However, they will probably not be able to transfer to pyrene because of steric constraints (only one pyrene molecule can dock with THQ at a time). Therefore, the hydrogen will be released from THQ as molecular hydrogen.

As pressure increases to 1000 and 1500psi, efficiency increases past 100% and approaches 130% at 1500psi. This means that gas phase hydrogen is being utilized in the hydrogenation of pyrene. Quinoline produced by the dehydrogenation of THQ is being hydrogenated by the gas-phase hydrogen back to THQ. This H-shuttling mechanism can explain the >100% efficiency.

Figure 6 shows how pyrene conversion and THQ conversion varies with reactant ratio at 425°C, 120 minutes reaction time and inert atmosphere. The figure shows that increasing the solvent ratio to 20:1 increases the conversion of pyrene with respect to THQ. At 425°C, pyrene hydrogenation is thermodynamically limited to a maximum conversion of 36% under these conditions (20:1 molar ratio). At 2:1 molar ratio, the reaction is limited by the availability of transferable hydrogen, which limits conversion to 24%. The thermodynamic limitation can be overcome by dropping the temperature to 400°C, but this will have an effect on the kinetics of the transfer of hydrogen from THQ to pyrene. Experimentation has shown that it takes 120 minutes more reaction time at 400°C to reach the same conversion level seen at 425°C. It will be necessary to make a trade-off between reaction temperature, reaction time and the solvent/resid ratio. This will depend on how good the final product needs to be, and the economics of the process.

CONCLUSIONS

This study has shown that polar H-donors such as THQ and indoline are good solvents for upgrading petroleum resids. Model compounds studies using pyrene have shown that THQ is a better donor in terms of amount of conversion of the solvent with respect to the model compound. This will be an important aspect of future research as any process involving H-donors will have to consider the recycle of the solvent, i.e., rehydrogenation. THQ also acts as a H-shuttler between the gas phase and the reactant.

It was found from research undertaken using a large batch reactor, that a hydrogen consumption level of 4400 scf/bbl will be required to get a 90% conversion of the resid to <1000°F boiling material. This will also increase heteroatom removal but further hydrogenation will have to be done on the product to get the sulfur levels to less than 1%.

Studies undertaken in smaller microautoclaves have shown that an increase in H/C ratio of 25% is possible (1.62 is maximum obtained using THQ and 1000psi hydrogen pressure). From the SIMDIST data, asphaltene conversion data, and elemental analysis, a potential trade-off between cracking and hydrogenation of both the heavy asphaltene molecules and the lighter boiling material is envisioned. Because this system is non-catalytic, it will not be possible to get high cracking and high hydrogenation levels. The final process should be determined based on the required final product, e.g., does the product only need to be good enough for feeding to the FCC?

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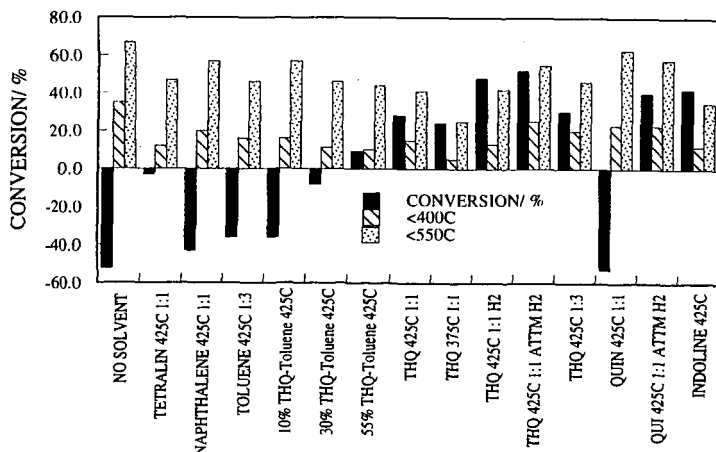


Figure 1. Effect of various solvents and reaction conditions on upgrading vacuum residue: 1 hour reaction time

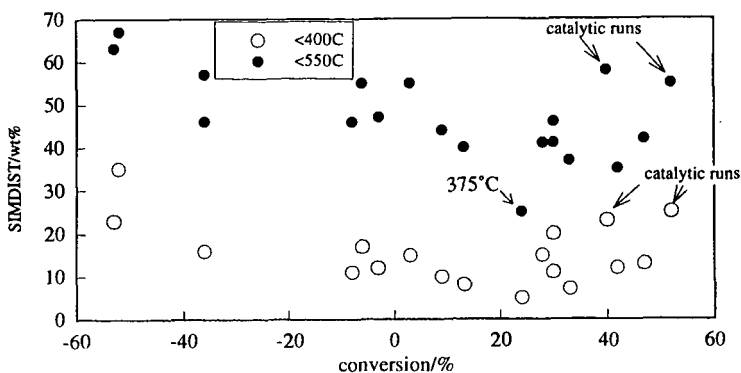


Figure 2. Vacuum resid conversion of asphaltene vs. SIMDIST results: various reaction conditions

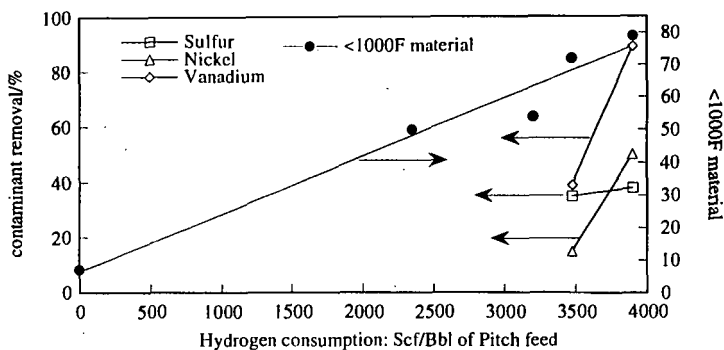


Figure 3. Conversion of ROSE pitch to <1000°F material and removal of contaminants vs. H-consumption: THQ and indoline

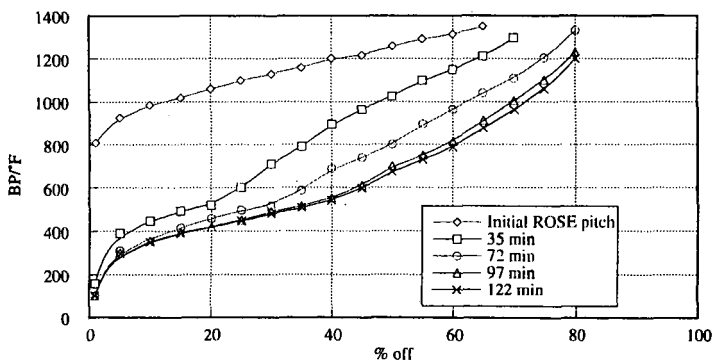


Figure 4. Boiling point distribution for products from THQ hydrogen donation to ROSE pitch: effect of donation time at 425°C, 2:1 solv/resid, 1000psi H₂

Table 1. Effect of temperature, hydrogen pressure and reaction time on conversion of ROSE pitch and THQ, and H/C ratio of products.

Feedstock	Temperature/ °C	H ₂ Pressure/ psi	time/ min	<800°F %	<1000°F %	Asphaltene Conv./%	THQ Conv./%	H/C
ROSE pitch	-	-	-	2	9	-	-	1.27
ROSE pitch	375	0	60	7	18	12	-	1.46
ROSE pitch	400	0	60	9	23	17	-	1.54
ROSE pitch	425	0	60	18	38	33	-	1.51
ROSE pitch	450	0	60	40	64	24	-	1.55
ROSE pitch	425	500	120	32	55	32	53	1.55
ROSE pitch	425	1000	120	32	55	36	33	1.62
ROSE pitch	425	1500	120	29	50	40	36	-
ROSE pitch (oil)	-	-	-	5	8	-	-	1.33
ROSE Pitch (asphaltene)	-	-	-	0	2	-	-	1.09
ROSE pitch (oil)	425	1000	120	24	44	-	-	1.70
ROSE pitch (asphaltene)	425	1000	120	8	36	-	-	1.40

Table 2. Effect of various donor/non donor solvents on pyrene conversion : 425°C, 1000 psi hydrogen pressure

Model Compound	Solvent	mol/mol	Time/ min.	pyrene conversion/%	solvent conversion/%
pyrene	acridine	2	60	8.5	83
pyrene	acridine	2	120	13.7	95
pyrene	pyrrolidine	2	120	13.1	-
pyrene	tetrahydrocarbazole	2	120	16.3	18
pyrene	indoline	2	60	47	48
pyrene	indoline	2	120	47	78
pyrene	toluene	2	120	7.4	-
pyrene	THQ	2	60	32	12
pyrene	THQ	2	120	32	14
pyrene	octahydroacridine	2	60	17	2
pyrene	octahydroacridine	2	120	22	12

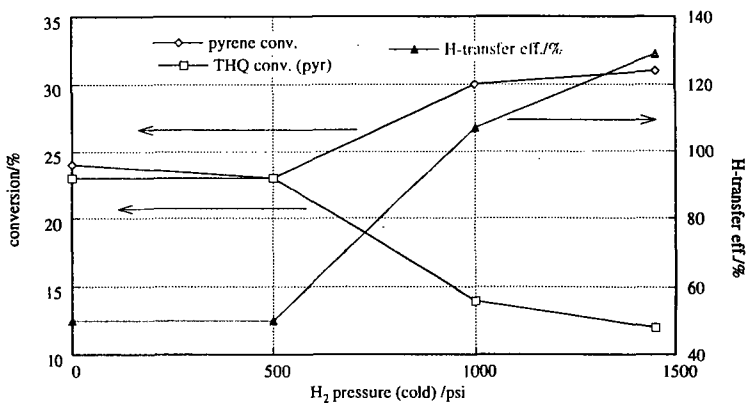


Figure 5. Pyrene/THQ conversion and H-transfer efficiency vs. H₂ pressure: 425°C, 120min

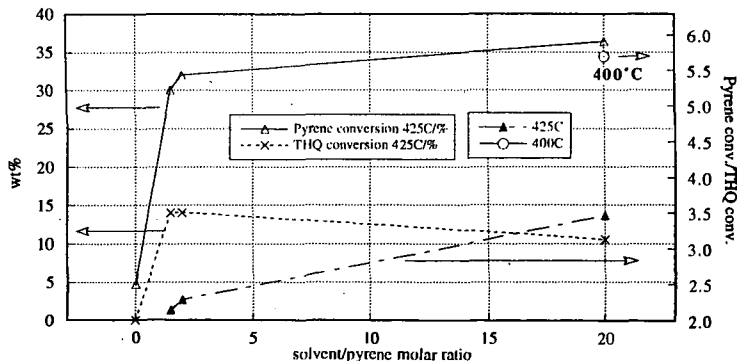


Figure 6. Pyrene and THQ conversion vs. reactant ratio : 425°C, 120 minutes, 1000psi H₂